OPTIMIZING ELECTROCOAGULATION PROCESS FOR TREATMENT OF BIODIESEL WASTEWATER USING RESPONSE SURFACE METHOD

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Submitted by:

Damber Bdr Powrel
110CH0642

Under the supervision of
Dr. PRADIP RATH

Department of Chemical Engineering
National Institute of Technology, Rourkela
Rourkela – 769008

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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the project entitled, "**OPTIMIZING ELECTROCOAGULATION PROCESS FOR TREATMENT OF BIODIESEL WASTEWATER USING RESPONSE SURFACE METHOD**" submitted by **Damber Bdr Powrel** in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date: 4/07/2014

Dr. P Rath

Department of Chemical Engineering

National Institute of Technology

Rourkela – 769008, Odisha

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Date: 4/07/14 Damber Bdr Powrel

ABSTRACT

The objective of this research was to determine the optimum conditions for the biodiesel waste water treatment using electrocoagulation process.

Biodiesel, which is, mono alkyl esters of long-chained fatty acids, is an alternative fuel for diesel engines. It is produced by the chemical reaction of vegetable oil or animal fat with an alcohol. Commercial biodiesel production employs an alkali-catalyzed trans-esterification reaction method. This method ensures a high production of biodiesel from oil by a basic chemical reaction within a short period of time. In this process water is used to wash off impurities which is repeated 2–5 times depending on the quantity of impurities in the methyl-ester. The amount of wastewater generated in the process is very huge (20–120L per 100L of biodiesel). The wastewater is basic in nature, and contains high amounts of oil and grease.

Conventional flotation techniques like Dissolved Air Floatation technique (DAF) and an oil and grease (O&G) trap unit are not good enough for removing oil emulsions without pretreating with chemicals. Electrocoagulation (EC) has, therefore, been successfully used to treat numerous wastewaters.

An EC reactor is composed of an electrolytic cell with a pair of electrodes immersed in the wastewater that serves as the electrolyte. The process of pollutant removal involves the application of an electric current to electrodes which in turn leads to the dissolution of metal ions, such as iron or aluminum, from a sacrificial anode. Consequently, the metallic hydroxide, a coagulant formed by oxidation in the electrolyte in an aqueous phase, destabilizes colloidal suspension such as emulsified oil. Further, the destabilized colloids aggregate and form flocks. Finally, these colloid-adsorbed flocks can be separated by sedimentation or by floatation.

In short, the EC process involves three main mechanisms for pollutant removal, i.e., electrode oxidation, gas bubble generation, and flotation and sedimentation of formed flocks.

The main pollutants to be removed are COD, O&G, and suspended solids. Three important electrochemical factors are tested: initial pH, applied voltage, and reaction time. Response surface methodology (RSM) is used to get a set of designed experiments to obtain optimal multifactor operating conditions for the EC process. Response Surface Methodology explores the relationships between several explanatory variables and one or more response variables. It is a collection of mathematical and statistical techniques for empirical model building. The main objective is to optimize a response (output variable) which is influenced by several independent variables (input variables).

Key Words: Biodiesel, Electrocoagulation (EC), Response Surface Method (RSM),

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INTRODUCTION

Biodiesel, as the only biofuel that can be used for the diesel engine, was developed in last decades because of limited energy resources and the huge increase in energy demand. Biodiesel is one of the most promising alternative fuels, mainly because its price is comparable with standard diesel. Biodiesel, is produced by the chemical reaction of vegetable oil or animal fat with an alcohol. Government in Thailand has promoted the use and the production of biodiesel as a alternative diesel fuel to lower the importation of oil and promote the use of alternative energy available from domestic crops. In Thailand, the raw material used for the biodiesel production is palm oil and it is produced by using alkali catalyst for trans-esterification reaction. This method ensures a high production of biodiesel by a simple chemical reaction which occurs within a short period of time. Large amounts of water is used for washing impurities. The wastewater is basic in nature. Biological treatment of the biodiesel wastewater is generally very difficult. Conventional flotation techniques like Dissolved Air Floatation technique (DAF) and an oil and grease (O&G) trap unit are not good enough for removing oil emulsions without pretreating with chemicals. Electrocoagulation (EC) has, therefore, been successfully used to treat numerous wastewaters.

The addition of aluminum or ferric salts, highly charged cations, can enhance the destabilization of an oil-water emulsion when applying with DAF. There are studies on treatability of vegetable oil industry effluents using the DAF technique with lime, alum, or ferric chloride as chemical coagulants. Their results showed that ferric chloride was the most effective coagulant in reducing chemical demand (COD) and O&G. Physicochemical methods appear to be effective in

removing O&G from oily wastewater, but they require working with chemicals, and their operations are sometimes complicated.

Electrocoagulation process has been extensively and successfully used for the treatment of numerous wastewaters including municipal wastewater, dying wastewater, and wastewater containing organic species such as phenol. An EC reactor is composed of an electrolytic cell with a pair(s) of electrodes immersed in a liquid (wastewater) that serves as the electrolyte. The process of pollutant removal involves the application of an electric current to sacrificial electrodes which in turn leads to the dissolution of metal ions, such as iron or aluminum, from a sacrificial anode. Consequently, the metallic hydroxide, a coagulant formed by electrolytic oxidation in an aqueous phase, destabilizes colloidal suspension such as emulsified oil. Further, the destabilized colloids aggregate and form flocs.

With aluminum as an anode, the electrochemical reactions is as follows:

Anode reactions: $Al_{(s)} \rightarrow Al^{3+}{}_{(aq.)} + 3e^-$ (1)

Cathode reaction: $H_2O + 2e^- \rightarrow H_{2\,(g)} + 2OH^-$ (2)

Solution/electrolyte: $Al^{3+}{}_{(aq.)} + 3H_2O \rightarrow Al\,(OH)_{\,3} + 3H^+$ (3)

Finally, these colloid-adsorbed flocs can be easily separated by sedimentation or by floatation with air. In short, the EC process involves three main mechanisms for pollutant removal, i.e., electrode oxidation, gas bubble generation, and flotation and sedimentation of formed flocs. Electrocoagulation process has large number of advantages such as: it provides a fast rate of

pollutant removal and simplicity of operation; no chemical additive is required, produce less amount of sludge.

These advantages of EC makes it more favorable than other physicochemical treatment processes. Recently, EC has also been successfully applied to remove oil and COD from the oily wastewater that comes from restaurants and the mechanical and metallurgical industries.

In this study, EC process using a graphite cathode and an aluminum anode is used for treatment the oily wastewater from the biodiesel production processes. The pollutants to be removed are COD, O&G, and suspended solids (SS). Here three important electrochemical factors were tested: **initial pH, applied voltage, and reaction time.** Response surface methodology was employed to generate a set of designed experiments to obtain optimal multifactor operating conditions for the EC process. RSM is considered to be an effective means to design experiments that help to reduce the number of experimental trials, to assess the relative significance of variables and their interactions, and to build model. Finally, a full quadratic model for prediction of pollutant removal efficiency can be developed and verified with experimental data.

1. LITERATURE REVIEW

1.1 ELECTROCOAGULATION (EC)

Electrocoagulation involves the passing of electric current through water/wastewater. This process has proven to be very successful in the removal of pollutants. People have been using electrocoagulation systems for many years. Different types and shapes of electrodes, like plates, wire mesh, balls, rods, fluidized bed spheres and tubes can be used for this process. In London the first plant was built in 1889 for treating sewage.

The electrocoagulation process is based on the responses of pollutants to strong electric fields and electrically induced oxidation and reduction reactions. Depending on the solution, this process can take out over 99% of some cations and can also disrupt cell wall or cell membrane of microorganisms in the wastewater. It can be used to precipitate colloids and remove huge amounts of other ions and emulsions. It can also be used for the purification of drinking water by removing pathogens and heavy metals.

Coagulation is a process used to destabilize small particles and aggregate into larger particles. Water pollutants such as ions of heavy metals and other colloids are held in the solution by some electrical charges. In the year 1882, Schulze, showed that to destabilized the colloidal systems ions having a charge opposite to that of the colloid was to be added, and this can be aggregated and separated by sedimentation and filtration processes.

There are two types of coagulation process, Chemical coagulation which employs chemical coagulants for coagulation and Electrocoagulation which employs strong electrical field to coagulate. But chemical coagulation has lots of disadvantages like higher costs for chemical coagulants and treatments, large amount of sludge formation, and harmful waste products. The sludge produced contains large amount of bound water which are very difficult to dewater and filter.

There are few similarities between electrocoagulation mechanism and chemical coagulation, but the characteristics of the floc formed by the two different mechanisms differ greatly from each other. An electro-coagulated floc contains less bound water, has more shear resistance, and it is more easily filterable. Electrocoagulation process can reduce water pollutants by as much as 98% and lower the treatment cost by 90% for wastewater containing heavy metal ions and oil emulsions.

1.2 RESPONSE SURFACE METHOD

One of the most important feature of Response Surface Method is the design of experiments (DoE). Originally, these strategies were developed for the model fitting of physical experiments, but it is also applicable to numerical experiments. The main aim here is the selection of the points where the response (output) should be evaluated.

For designing optimal experiments, the criteria are mostly associated with the mathematical model of the process, which are polynomials with an unfamiliar structure and therefore, the corresponding experiments are designed only for every particular problem. The accuracy of the

estimation and the cost of building the response surface highly depend on the choice of design of experiments.

When we are sure that the design variables chosen initially have very less or no effect on the response, then screening experiments are performed mostly in the early stages of the process. This is the method followed in a traditional Design of Experiments. The main objective is to find the design variables that have huge effects in further investigation. Genetic Programming has shown good screening properties, which tells us that the selection of the appropriate design variables and the identification of the model can be both carried out together at the same time.

A particular combination of trails defines an experimental design and the possible settings of each independent variable in the N dimensional space are called levels.

1.2.1 Full factorial design

To investigate all possible combinations and to develop an approximation model that can express interactions between N design variables, a full factorial approach may be required. Instead of varying one variable at a time, all design variables are varied together in a factorial experiment. In the optimization problem, the lower and upper bounds of each of N design variables needs to be defined. The permissible range is then discretized at different levels. If each of the variables is defined at only the lower and upper bounds (two levels), the experimental design is called 2N full factorial and if the midpoints are also included, the design is known as 3N full factorial as shown in Figure 1.

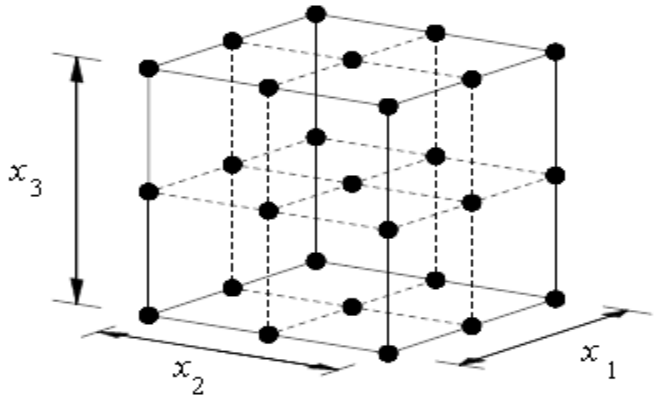

Fig1: A 3^3 full factorial design (27 points)

For fitting second-order models, factorial designs can be used. A second-order model can be used to improve the optimization process if a first-order model lacks of fitting because of the interaction between surface curvature and variables. A second-order model is defined as given below

$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{\substack{i=1 \\ i<j}}^{n} a_{ij} x_i x_j$$

Where X_i and X_j are the design variables and "a" are the tuning parameters.

To develop a quadratic response surface model in N variables, we need to study at three levels so that the tuning parameters can be estimated. Therefore, evaluation of at least (N+1) (N+2) / 2 function will be necessary. The number of experiments usually grows exponentially (3N for a full factorial) and becomes impractical for a higher number of variables. Commonly, a full factorial design is used for five or lesser than five variables.

For this particular project, Box-Behnken design, is used to get a set of designed experiment using MINITAB 16 software. Minitab is a statistics package. Researchers Barbara F. Ryan, Thomas A. Ryan, and Brian L. Joiner in 1972 developed the software at the Pennsylvania State University.

1.3 CHEMICAL OXYGEN DEMAND (COD)

The measurement of the amount of O_2 in water utilized for chemical oxidation of contaminants is known as COD. This test is used to indirectly measure the amount of organic compounds in water samples. The main application of COD is to determine the amount of organic contaminant found in surface water or wastewater, thus, COD is an important measure of water quality and purity. The unit of COD is mg/L, which shows the mass of O_2 consumed per liter of solution.

COD has a great environmental significance. COD values are important in determining and controlling losses to sewer system. The BOD to COD ratio are useful in finding the purity and safety of wastewater. The ratio greater than 0.8 implies that the sample is highly polluted and needs biological treatment.

The principle of COD is simple. In the presence of H_2SO_4, Silver Sulphate and Mercuric Sulphate the organic compounds present in the sample becomes fully oxidized by $K_2Cr_2O_7$. By refluxing the sample with known quantity of $K_2Cr_2O_7$ in the H_2SO_4 medium, the excess $K_2Cr_2O_7$ can be found out by titrating it against freshly prepared ferrous ammonium sulphate solution. Ferroin is used as an indicator. Now $K_2Cr_2O_7$ consumed by the sample will be equivalent to the amount of O_2 needed to oxidize the organic compounds.

2. MATERIALS AND METHOD

2.1 TEST WATER

The test water for the experiments were prepared with the following composition:

Table 1. Composition of wastewater

Component	Value
Water	1 L
Diesel Oil(O&G)	6020 mg/L
Methanol	10667 mg/L
Glycerol	1360 mg/L
Suspended Solids(SS)	340 mg/L

The wastewater thus prepared had the following properties:

Table2. Characteristics of wastewater

Characteristics	Value
COD	1856 mg/L
pH	6.8
O&G(Oil and Grease)	6020 mg/L
SS(Suspended Solids)	340 mg/L

2.2 EXPERIMENTAL APPARATUS

Figure 2 shows a diagram of the experimental apparatus. Electrocoagulation experiments was conducted in a 2L batch reactor. A graphite cathode and an aluminum anode with flat and rectangular shapes were placed in parallel and vertically, with a separation distance of 1.5 cm. The electrode gap was maintained constant in all experiments.

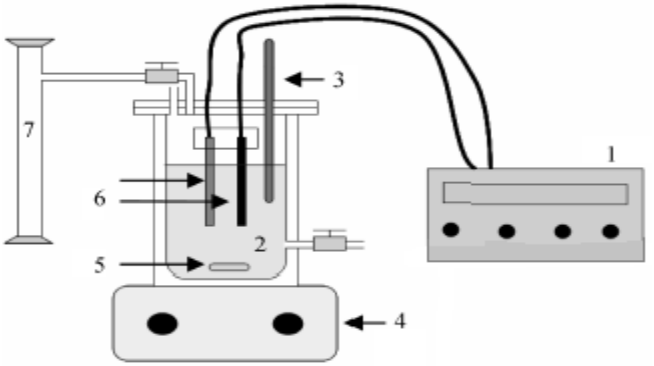

Fig.2. Experimental apparatus. (1) DC power supply; (2) electrolyte; (3) Thermometer; (4) stirrer plate; (5) magnetic bar; (6) electrodes; (7) Gas collection equipment.

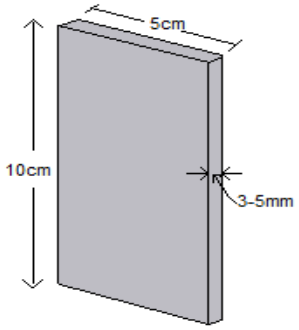

Fig.3: Electrode dimensions

The reaction surface area of each electrode was 50cm^2 (10*5*0.5). The electrodes were connected to a digital DC power supply of 0–60 V. The test volume of wastewater for each trial was 1 L. All experiments were conducted at the room temperature.

2.3 EXPERIMENTAL DESIGN

The Box-Behnken design, an experimental design for RSM, was used to get a set of designed experiments by MINITAB software (version16). This design was developed based on the combination of a two level (full or fractional) factorial design with an incomplete block design. Keeping other factors or variables constant at central values, a certain number of factors are put through all possible combinations. Here, the Box-Behnken design is used for 3 factors: initial pH (X_1), applied voltage (X_2), and reaction time (X_3), involving three blocks. Two factors/ variables were put through the four possible combinations of high and low in each block.

Using MINITAB software, fifteen experimental trails were designated. Response surface regression analysis was performed by fitting experimental data to a full quadratic model, providing regression coefficients. The quadratic model is expressed by the equation given below:

$$Y_i = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4n} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} X_{ij} \qquad \textbf{(1)}$$

Where, β_0, β_i, β_{ii} and β_{ij} are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively; and X_i, and X_{ij} are the independent variables. Response (Y_i) represents the percentage removal of COD (Y_1), O&G (Y_2), and SS (Y_3).

3. EXPERIMENTAL PROCEDURES

3.1 EFFECTS OF PARAMETERS

The experimental apparatus was set-up as shown in figure 4.

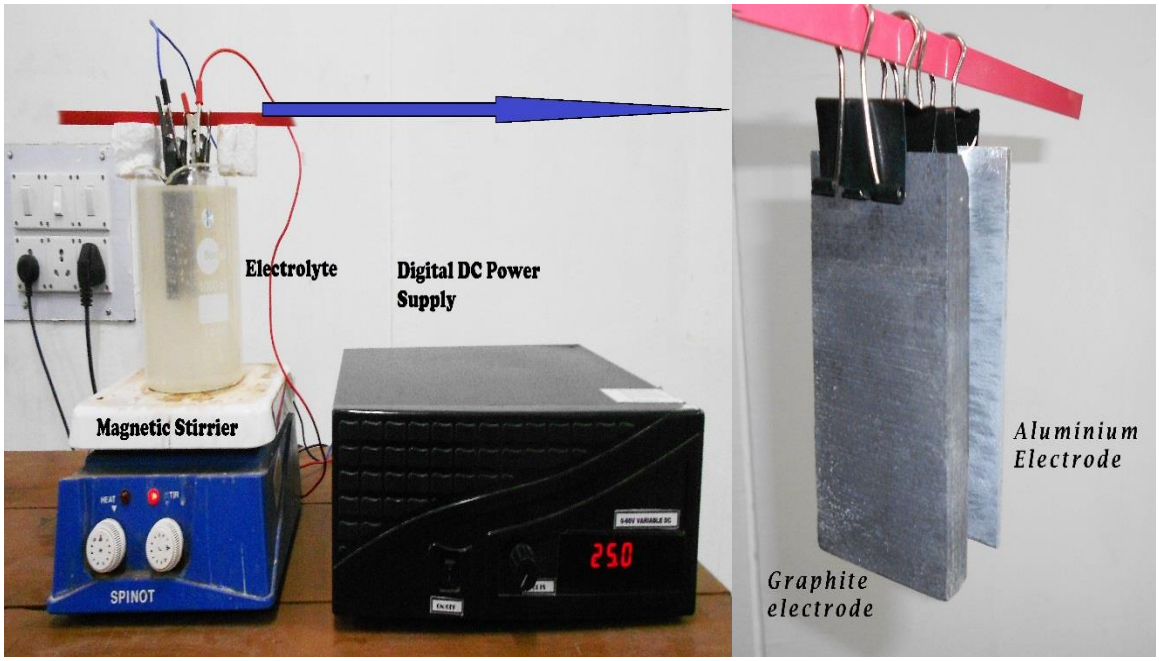

Fig4. Experimental setup

The wastewater for the experiments was prepared as given in Table 1 and various characteristics of wastewater was determined as shown in Table 2. All the experiments were conducted at room temperature.

To determine the ***effect of Initial pH,*** the pH of the wastewater was adjusted to 4, 6 and 9 using either H_2SO_4 or NaOH. In each of the experimental run, the applied voltage was kept constant at 20V and a constant reaction time of 30 minutes. After 30 minutes each of reaction time, the treated wastewater for tested for COD, O&G and SS as per the procedure given in the preceding

pages. A graph was plotted for % Removal vs Initial pH for various characteristics. Optimum value of pH was found out from the graph.

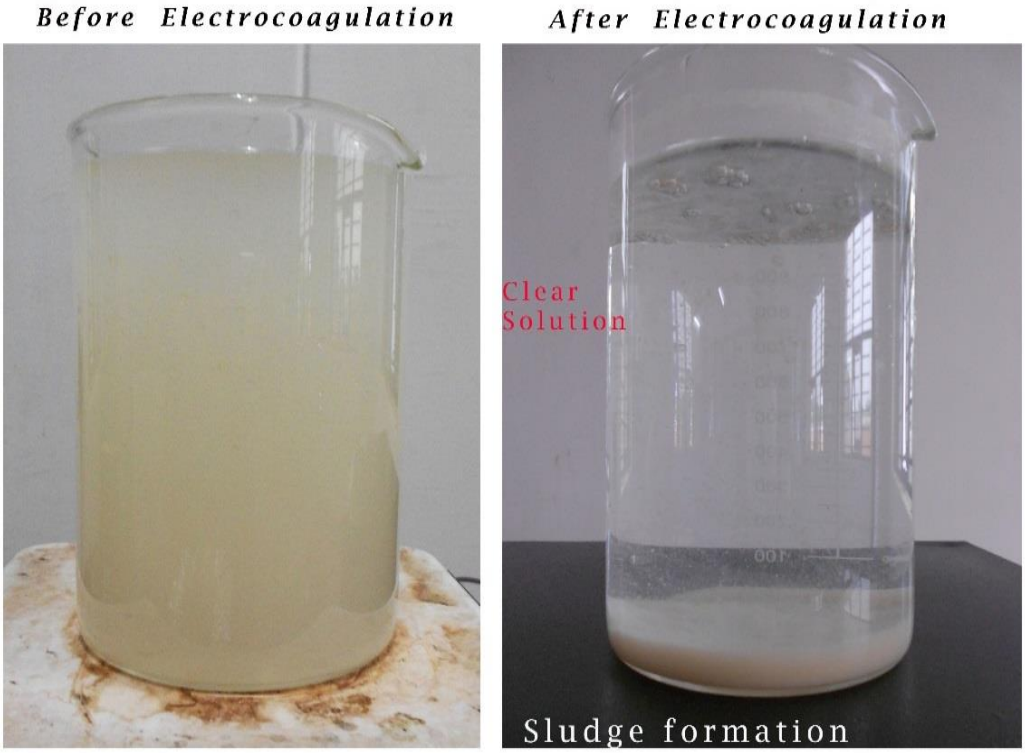

Fig5. Wastewater before and after electrocoagulation

To determine the ***effect of Applied Voltage***, the applied voltage was varied from 10 to 30V while the reaction time was kept constant at 30 minutes. The value of pH for this was the optimum value determined in step 7. After 30 minutes each of reaction time, the treated wastewater for tested for COD, O&G and SS as per the procedure given in the preceding pages. A graph was plotted for % Removal vs Applied Voltage for various characteristics. Optimum value of applied voltage was found out from the graph.

To determine the ***effect of Reaction Time,*** the optimum values of pH and applied voltage as determined earlier were taken while the reaction time was varied from 10 to 40 minutes. The treated wastewater for tested for COD, O&G and SS as per the procedure given in the preceding pages. A graph was plotted for % Removal vs Reaction Time for various characteristics. Optimum value of Reaction Time was found out from the graph.

3.2 BOX-BEHNKEN DESIGN

Box-Behnken design was used to create 15 different sets of experimental trails for various values of initial pH, applied voltage and reaction time using MINITAB software. Experimental procedures were carried out as discussed above.

To develop a Response Surface Regression Model, a full quadratic model (equation (1)) was applied to the experimental observations of removal efficiencies.

3.3 CHEMICAL OXYGEN DEMAND (COD)

3.3.1. Preparation of Reagents

Standard Potassium Dichromate Reagent

4.913g of dry potassium dichromate was taken in a clean and dry beaker. Exactly 33.3g of mercuric sulphate was added to the same beaker. About 167ml of concentrated sulphuric acid was added to the same beaker and the contents were properly dissolved. When cooled the volume was made upto 1000ml using distilled water.

Sulphuric Acid Reagent

Exactly 5.5g of silver sulphate crystals was taken in a dry and clean beaker. Carefully, 500ml of concentrated H_2SO_4 was added to it. The contents was allowed to stand for 24 hours to ensure complete dissolving of the crystals.

Standard Ferrous Ammonium Sulphate Solution

Exactly 39.2g of Ferrous Ammonium Sulphate crystals was taken in a dry clean beaker. It was dissolved in 1000ml of distilled water. This solution was to be freshly prepared for titration.

3.3.2. Testing of Sample

Exactly 2.5ml of sample or blank (distilled water) was taken in a clean dry conical flask and it was diluted with 50ml of distilled water. Using a pipette, 12.5ml of Potassium Dichromate solution was added to it. The contents were properly mixed and carefully, 12.5ml of Sulphuric Acid Reagent solution was added to it. The contents were hot then. The conical flask was then connected to a condenser and it was refluxed for 2 hours at 150^0C. Meanwhile, Standard Ferrous Ammonium Sulphate solution was prepared and transferred to a burette. After boiling for 2 hours, it was allowed to cool to room temperature. Few drops of Ferroin Indicator solution was added. The colour of the solution turned bluish-green. It was titrated against the Ferrous Ammonium Sulphate solution taken in the burette. The end point was change of colour from bluish-green to reddish-brown. The volume of the Ferrous Ammonium Sulphate solution consumed was noted.

3.3.3 Calculations

The COD of the sample was calculated as follows:

$$COD = \frac{(\mathrm{A} - \mathrm{B} * \mathrm{N} * 8 * 1000)}{Vs}$$

Where,
A= Volume of the Ferrous Ammonium Sulphate for Blank

B= Volume of Ferrous Ammonium Sulphate for sample

N= 0.1 (Normality of Ferrous Ammonium Sulphate)

V_s= Volume of the sample taken

3.4 OIL AND GREASE BY HEXANE EXTRACTION METHOD

In a clean and dry conical flask containing 3–5 boiling chips was taken and its weight was measured. Two aliquots of sample was taken in separate bottles with 250ml volume in each. The first 250ml sample was poured into the separatory funnel. 30 mL of n-hexane was poured to the sample bottle to rinse all interior of the bottle and poured into the separatory funnel. The sample was extracted by vigorously shaking the separatory funnel for 2 minutes with periodic venting to release excess pressure. The organic phase was allowed to separate from the aqueous phase for at least 10 minutes.

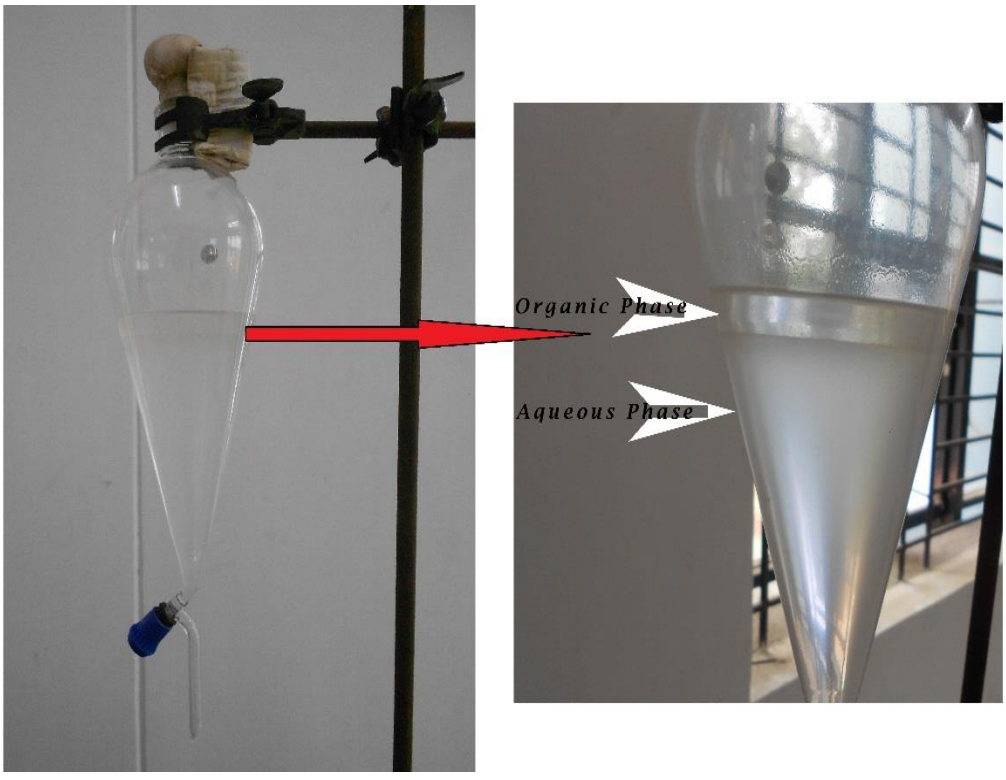

Fig6. Separatory Funnel

The aqueous layer (lower layer) was then drained out and discarded. Next the sample from the second bottle was poured into the separatory funnel. Again 30ml of n-hexane was poured to the bottle to rinse its interior and poured it into the separatory funnel. The extraction was done by shaking the separatory funnel for 2 minutes. The two phase was allowed to separate for 10 minutes. The aqueous layer (lower layer) was drained out and discarded. A small amount of the organic layer was also drained out to minimize the amount of water remaining in the separatory funnel. A filter paper with roughly 10 g of anhydrous Na_2SO_4 was placed in a funnel.

The n-hexane layer (upper layer) was drained into the pre-weighed conical flask through the Na_2SO_4. A water bath with temperature maintained at 70^0C was prepared and the flask containing the boiling chips was placed in it. When the flask appeared almost dry, the flask was removed from the hot bath while it still contained roughly 2 mL of residual liquid. Outer surface of the conical flask was wiped dry to remove moisture and oily fingerprints and placed the flask in a hood until visible dryness was achieved while cooling at room temperature. The weight of the flask was measured accurately. HEM (Hexane Extractible Material) (W_h) was determined by subtracting the two weights of the conical flask; tare weight and the total weight.

Concentration of Oil and Grease (O&G) in the sample was calculated from equation given below:

$$HEM\ (\frac{mg}{L}) = \frac{\mathrm{Wh}}{Vs}$$

Where, W_h = weight of the extractible materials

V_s = Vol. of the sample taken (0.5L)

3.5 SUSPENDED SOLIDS BY GRAVIMETRIC METHOD

A clean dry pre-weighed filter paper was placed in a funnel and the treated wastewater was filtered through it. After filtration, the filter paper was dried and the weight was measured accurately.

The amount of suspended solids was measured by subtracting the weight of the filter paper from the tare weight.

4. RESULTS AND DISCUSSION

4.1 EFFECT OF PARAMETERS

4.1.1 Effect of Initial pH:

Applied Voltage and Reaction Time were kept constant at 20V and 30mins, respectively.

Initial pH	% Removal		
	COD	O&G	SS
4	75.86	95.68	91.18
6	**79.3**	**97.67**	**94.11**
9	67.24	92.36	92.64

Table 3. Effect of Initial pH

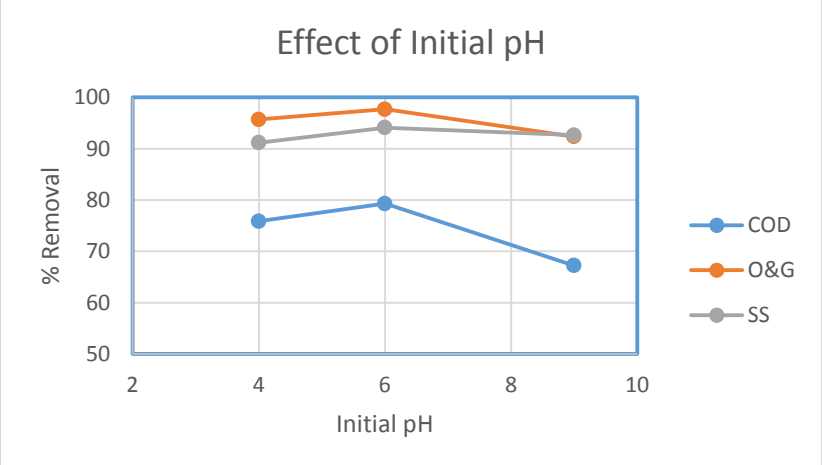

Fig 7. Effect of Initial pH

Figure 7 shows the effect of Initial pH on removal of pollutants. The maximum removal of pollutants is achieved at an initial pH of 6 at 79.3% COD, 97.67% O&G and 94.11% SS. The figure suggests that the pollutant removal is best achieved in the acidic condition and as the pH is increased to 9, the pollutant removal decreases further more because of less formation of reactive flocs of Aluminium Hydroxide.

4.1.2 Effect of Applied Voltage:

Initial pH and Reaction Time were kept constant at 6 and 30mins, respectively.

Table 4. Effect of Applied Voltage

Applied Voltage (V)	% Removal		
	COD	O&G	SS
10	58.62	78.47	94.11
15	63.79	78.53	92.65
20	79.3	97.67	94.11
25	**82.75**	**97.9**	**95.59**
30	70.69	88.57	95.59

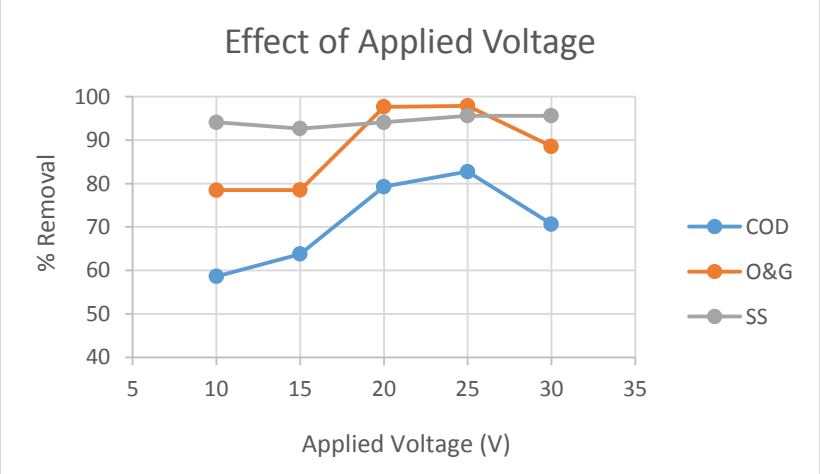

Fig 8. Effect of applied Voltage

As shown in the Figure 8, the pollutant removal efficiencies increased as the voltage was varied from 10 to 25 Volts. At an applied voltage of 25 Volts, maximum pollutant removal efficiency

was achieved at 82.75% COD, 97.9% O&G and 95.59% SS. As the voltage is further increased beyond 25V the removal efficiency decreases mainly because of the rise in pH of the solution and as shown earlier, the basic range of pH reduces removal efficiency of pollutants.

4.1.3 Effect of Reaction Time:

Initial pH and Applied Voltage were kept constant at 6 and 25V, respectively.

Table 5. Effect of Reaction time

Reaction Time (mins.)	% Removal		
	COD	O&G	SS
10	60.34	79.46	94.11
15	63.79	79.4	94.11
20	81.03	94.61	97.05
25	**84.48**	**98.2**	**97.05**
30	84.48	97.6	97.05
35	82.76	92.95	97.05

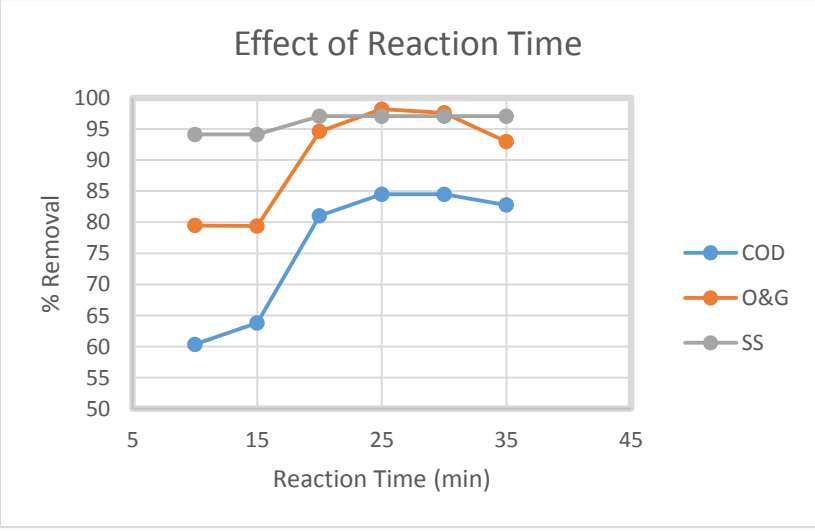

Fig 9. Effect of Reaction Time

As seen in the Figure 9, all the pollutant removal efficiencies increases as the reaction time is increased from 10 to 25mins. Maximum removal is achieved in 25mins of reaction time at 84.48% COD, 98.2% O&G and 97.05%SS. Beyond 25mins of reaction time, the pH of the solution increases to basic region, therefore, decreasing the removal efficiencies of pollutants.

4.2 BOX-BEHNKEN DESIGN EXPERIMENTS

Table 6 shows the Box-Behnken design with pH, Voltage and reaction time for fifteen experimental trails. To develop a response surface regression model, a full quadratic model (Equation (1)) was applied to the experimental observations of the removal efficiencies of COD (Y_1), O&G (Y_2) and SS (Y_3). The quadratic regression models are given below by the equations (2), (3), and (4).

$$Y_1 = -62.0626 + 16.7242X_1 + 4.83359X_2 + 2.41720X_3 - 0.862X_1^2 - 0.071125X_2^2 - 0.0392667X_3^2 - 0.2242X_1X_2 - 0.0344667X_2X_3 + 0.00288333X_3X_1 \quad \textbf{(2)}$$

$$Y_2 = -13.2924 + 13.8024X_1 + 3.45346X_2 + 1.96829X_3 - 0.9028X_1^2 - 0.0668X_2^2 - 0.0297556X_3^2 - 0.0635X_1X_2 - 0.0534X_2X_3 + 0.00786667X_3X_1 \quad \textbf{(3)}$$

$$Y_3 = 66.3043 + 6.6341X_1 + 0.55735X_2 - 0.15105X_3 - 0.5002X_1^2 - 0.\ 0129375X_2^2 - 0.00405X_3^2 - 0.0004X_1X_2 - 0.\ 0098X_2X_3 - 1.2738*10^{-18}X_3X_1 \quad \textbf{(4)}$$

Where X_1, X_2, and X_3 are the Initial pH, Applied Voltage and Reaction Time, respectively.

To verify the models, the sets of experiments shown in the table 6 were conducted. The table shows that there were no observable difference between the modeled and observed values.

Box-Behnken Design Experiment

Table 6. Box-Behnken Design Experiments.

Trail	Initial pH	Applied Voltage (V)	Reaction Time (mins)	COD Removal %			O&G Removal %			SS Removal %		
				Experimental	*Predicted*	*Residue*	*Experimental*	*Predicted*	*residue*	*Experimental*	*Predicted*	*residue*
1	4	10	25	56.89	56.46	0.43	78.2	80.02375	-1.82375	92.6	91.32625	1.27375
2	4	20	10	60.34	60.77125	-0.43125	79.47	80.88625	-1.41625	91.18	92.275	-1.095
3	4	20	40	75.86	71.98125	3.87875	95.68	93.61375	2.06625	91.18	91.9075	-0.7275
4	4	30	25	75.86	79.7375	-3.8775	95.68	94.50625	1.17375	92.64	92.09125	0.54875
5	6.5	10	10	55.17	55.16875	0.00125	79.27	76.03	3.24	94.11	94.28875	-0.17875
6	6.5	10	40	58.62	62.92875	-4.30875	82.15	82.3925	-0.2425	94.11	94.65625	-0.54625
7	6.5	20	25	81.03	81.03	0	98.24	98.24	-1.413E-14	97.05	97.05	0
8	6.5	20	25	81.03	81.03	0	98.24	98.24	-1.413E-14	97.05	97.05	0
9	6.5	20	25	81.03	81.03	0	98.24	98.24	-1.413E-14	97.05	97.05	0
10	6.5	30	10	70.68	66.37125	4.30875	85.22	84.9775	0.2425	95.58	95.03375	0.54625
11	6.5	30	40	75.86	75.86125	-0.00125	92.82	96.06	-3.24	95.58	95.40125	0.17875
12	9	10	25	72.41	68.5325	3.8775	79.33	80.50375	-1.17375	92.64	93.18875	-0.54875
13	9	20	10	60.34	64.21875	-3.87875	80.13	82.19625	-2.06625	94.11	93.3825	0.7275
14	9	20	40	70.69	70.25875	0.43125	88.33	86.91375	1.41625	95.58	94.485	1.095
15	9	30	25	68.96	69.39	-0.43	90.46	88.63625	1.82375	92.64	93.91375	-1.27375

The Residual Plots for COD, O&G and SS are given below by Figure 10, Figure 11 and Figure 12, respectively. The four-in-one residual plot displays four different residual plots together in one graph window. This layout is useful for comparing the plots to determine whether the model meets the assumptions of the analysis. The residual plots in the graph include:

- Histogram - indicates whether the data are skewed or outliers exist in the data
- Normal probability plot - indicates whether the data are normally distributed, other variables are influencing the response, or outliers exist in the data
- Residuals versus fitted values - indicates whether the variance is constant, a nonlinear relationship exists, or outliers exist in the data
- Residuals versus order of the data - indicates whether there are systematic effects in the data due to time or data collection order

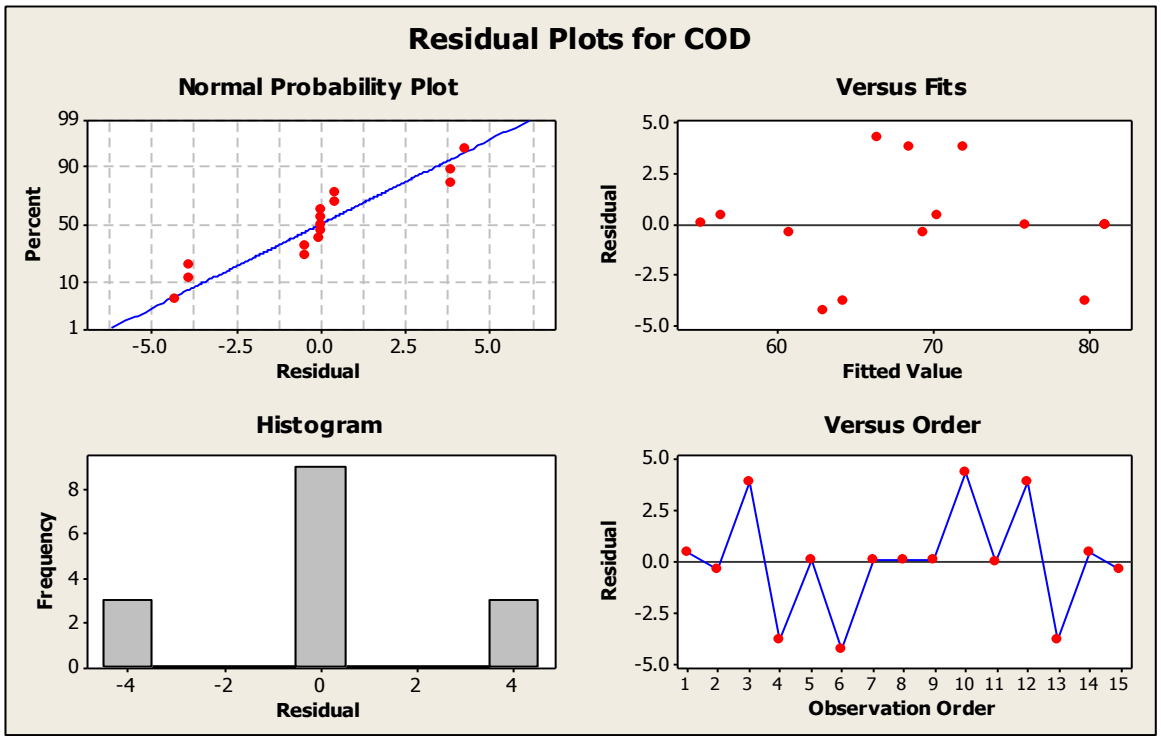

Fig 10. Residual Plots for COD

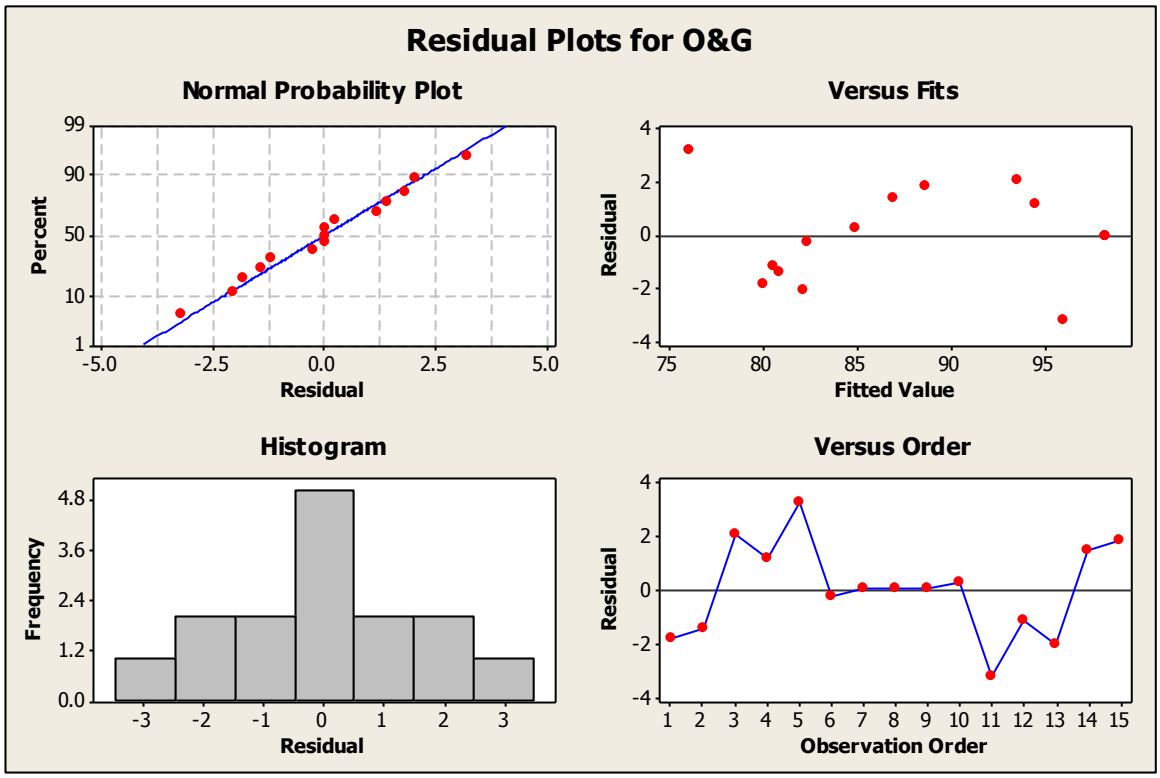

Fig 11. Residual Plots for O&G

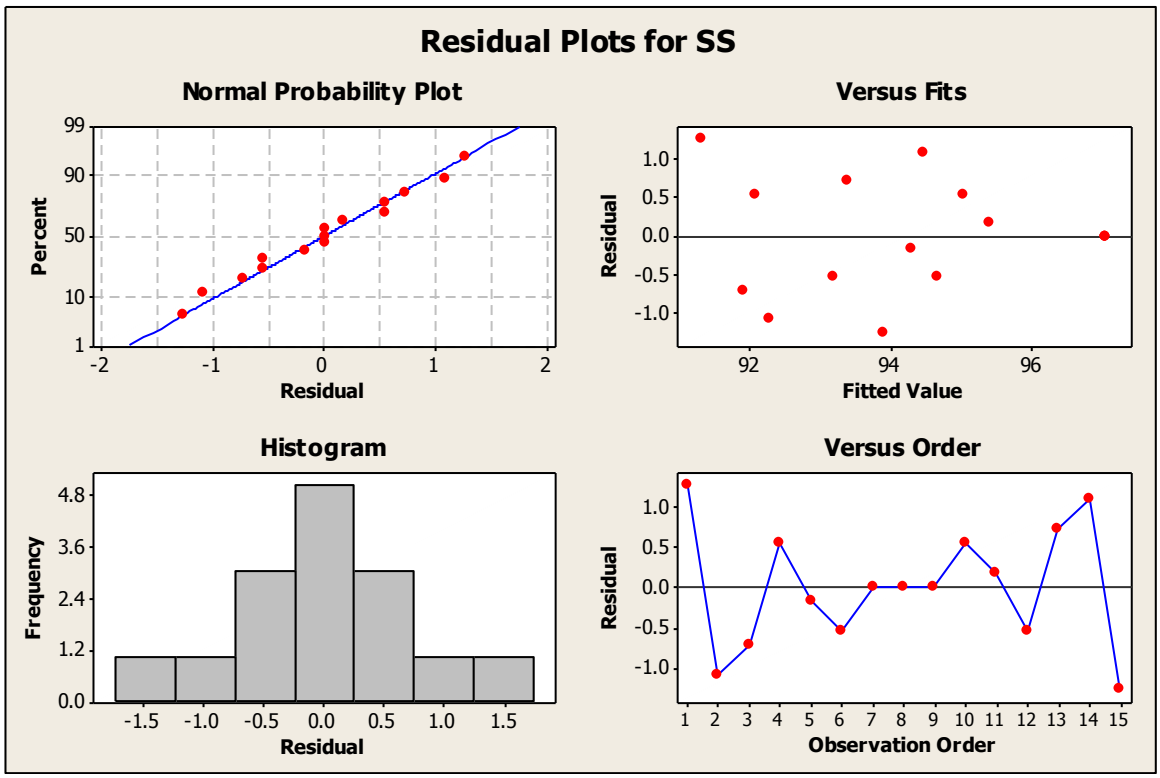

Fig 1. Residual Plots for SS

4.3 OPTIMIZED CONDITIONS

A comparison of optimum conditions and removal efficiencies obtained from one factor at a time experiments and Box-Behnken Design Optimization is given below in Table 7.

Table 7. Optimized Conditions

Characteristics	**Optimum Conditions**	
	One Factor at a Time Experiments	Box-Behnken Design Optimization
Initial pH	6	6.5
Applied Voltage (V)	25	20
Reaction Time (min)	25	25
COD removal (%)	84.48	81.03
O&G removal (%)	98.2	98.24
SS removal (%)	97.05	97.05

5. CONCLUSION

With the advancement in industrial revolution, treatment of industrial effluents has become a matter of great significance and priority as this is the key reason for various pollution and health hazards. Various government policies and standards have also been introduced to minimize the amount of pollutants an industry releases to the environment. Therefore, it is necessary to find a way to solve this problem such that it benefits both sides; the environment and the industry itself.

Although EC process is an effective process for biodiesel wastewater treatment, it however, requires a further biological treatment process the since COD removal achieved is comparatively less (81.03%) due to lesser removal of glycerol and methanol. Thus, the EC process is more suitable for primary treatment for biodiesel wastewater. Few earlier studies have demonstrated that pretreatment of oily wastewater with EC processing can enhance the biodegradability of oil emulsions in the wastewater. Therefore, a pretreatment with EC followed by a biological treatment process seems to be the best method for treating oily wastewater rather than evaporation or pure physicochemical treatments. Advantages of this method are; it has low energy consumption, it requires short process time, requires no addition of chemicals and lesser amount sludge production.

To make matter easier, the use of Box-Behnken design to create a set of experimental runs can reduce the number of runs/ trails needed to optimize the operating conditions. Box-Behnken provides sufficient data to fit the quadratic models for pollutant removals. The optimization of the models provides the optimum conditions of parameters at which an operation can be carried out, the parameters here being the initial pH, applied voltage, and reaction time. Therefore, RSM could be effectively adopted to optimize the operating multi-factors in complex EC processes.

6. BIBLIOGRAPHY

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